

Applicants: Donald R. Huffman, et al.

Serial No. 08/471,890

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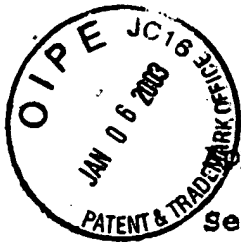
Group Art Unit: 1754

Title: SUPPLEMENTAL DECLARATION OF DONALD R. HUFFMAN UNDER 37  
C.F.R. §1.131 Dated May 10, 2000

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**TC 1700**



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al. Examiner: P. DiMauro

Serial No.: 08/486,669

Art Unit: 1754

Filed: June 7, 1995

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For: NEW FORM OF CARBON

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TC 1700

Assistant Commissioner for Patents  
Washington, DC 20231

SUPPLEMENTAL DECLARATION OF DONALD R. HUFFMAN  
UNDER 37 C.F.R. §1.131

Sir:

I, Donald R. Huffman, declare and say as follows:

1. I am a co-applicant of the above-identified application.
2. The other co-inventor of the above-identified application is Wolfgang Kratschmer, with whom I have collaborated. Although Dr. Kratschmer conducted his research at the relevant time at the Max Planck Institute in Germany, during the course of our collaboration, we have regularly communicated with one another, exchanging ideas, concepts and experimental details and results. In addition, we have visited each other's laboratories and have conducted additional research therein during our visits relating to the subject matter of the present invention described in the above-identified application. All of our combined activities have led to the completion of the invention described and claimed in the above-identified application.

3. I am currently a Regent's Professor of Physics, at the University of Arizona. I have received several accolades and awards relating to the subject invention, which include, inter alia, a Material Research Society Annual Medal Award in 1993, which I shared with Dr. Kratschmer, for the "Discovery of a Way to Produce Macroscopic Quantities of the Fullerenes and for Ellucidating (sic) Many of the Physical and Chemical Properties", and the Hewlett-Packard EuroPhysics Prize in 1994, which I shared with Drs. Kratschmer, Smalley and Kroto, for the "Discovery of New Molecular Forms of Carbon and their Production in the Solid State".

My curriculum vitae which lists, inter alia, my awards and honors and publications, is attached hereto as Exhibit A. (Exhs. A-1 to A-8).

4. It is my understanding that the United States Patent and Trademark Office cited a paper by Kratschmer, et al. published in Chemical Physics Letters, 1990, 167-170 ("Kratschmer, et al.") in support of a rejection of the above-identified application.

5. It is my understanding that Kratschmer, et al. published on July 6, 1990.

6. The invention described and claimed in the above-identified application was completed in the United States prior to July 6, 1990, i.e., the publication date of Kratschmer, et al.

7. The present invention is directed to a method of producing fullerene-60 and fullerene-70 as species of fullerenes in macroscopic amounts. An integral part of the present invention comprises vaporizing elemental carbon, e.g., graphite, in the presence of an inert quenching gas under conditions effective to form a soot comprising fullerenes, e.g., fullerene-60, which species of fullerenes are present in the sooty carbon product in macroscopic amounts. Proving that macroscopic amounts of fullerene species, e.g., fullerene-60, are present in the soot required isolation of the same from the soot. Thus, in addition to the step of producing species of fullerenes, e.g. fullerene-60, in macroscopic amounts, much of the activity described hereinbelow focused on proving that the species were produced in macroscopic amounts. Thus, we undertook to isolate fullerene-60 and fullerene-70, as species of fullerenes, from the soot.

8. As evidence that these acts, including the completion of the present invention in the U.S., occurred prior to the publication of Kratschmer et al., annexed hereto and made a part hereof are Exhibits B-I consisting of photocopies of laboratory records of experiments conducted in the laboratories at the University of Arizona.

9. The acts reported in the laboratory notebook entries were conducted prior to July 6, 1990, the publication date of Kratschmer, et al. either by myself or by someone working under my direction and control.

10. Data not pertinent to this invention and dates have been masked out in the preparation of these photocopies.

11. To enhance the understanding of the present process as to the acts described herein, reference is made to Exhibit B, which is a photocopy of 4 pages from Dr. Lowell Lamb's laboratory notebook, identified as Pages B-1 to B-4. Dr. Lamb, at the relevant time, was a graduate student working in my laboratory under my supervision and control.

12. Exhibit B summarizes in detail an embodiment of the present invention for producing fullerene species, e.g., fullerene-60, in macroscopic amounts. It describes that graphite rods are vaporized in an inert atmosphere of helium, e.g., 100 torr of helium, in a belljar apparatus. Above the rods is a chimney made out of a 2" diameter quartz tube topped with two microscopic slides to collect the vaporized carbon smoke. The carbon smoke is scraped off the chimney and sides of the chamber, and placed in benzene. The benzene is evaporated off until a brownish gold residue remains, then the brownish gold residue is sublimed in an atmosphere of inert gas such as helium. The sublimed material is collected on a quartz substrate. In each of the instances wherein the product was isolated, it was produced in amounts that could be seen with the naked eye.

13. One product of the procedure described hereinabove in paragraph 12 is a relatively pure fullerene-60 molecule in macroscopic amounts. This is verified by the UV-

VIS spectrum, in which one observes a camel structure in the absorption pattern, e.g., three specific absorptions at about 220, 270 and 340nm in the UV. Since the absorption between 240 and 270 nm reminded us (Kratschmer and myself) of camel humps, we designated the spectra as camel humps. (The three absorptions turned out to be associated with and is reflective of the presence of fullerene-60 and fullerene-70 in the sample).

14. An example of such a spectrum is depicted on pages B-3 and B-4, which are photocopies of additional pages in Lowell Lamb's notebook. Although the spectra are in color in the notebooks, the colors did not reproduce in the original photocopying. I have therefore retraced the lines with the appropriate colors on these pages of the exhibit and have written the appropriate color designations above and/or below the lines.

15. In the experiments described hereinbelow, the sooty carbon product was obtained by following the procedure outlined hereinabove. The emphasis in these experiments was to definitely prove that macroscopic amounts of fullerene species, e.g., fullerene-60, were produced. Thus, the emphasis in many of the exhibits is to separate the product produced in accordance with the procedure described herein from the soot and to show by measuring physical characteristics, such as UV spectra, IR spectra, X-ray diffraction pattern, and the like that the present process produced species of fullerenes, e.g.,

fullerene-60 and that they were produced in macroscopic amounts.

16. In the experiment described on pages B-3 and B-4, Lamb had followed the procedure described hereinabove and prepared fullerene species, e.g., fullerene-60, from soot, as described in paragraph 12. He had separated the fullerene products from the carbon sooty product by sublimation. More specifically, he had sublimed the mixed fullerene products, containing, among other things, fullerene-60 and fullerene-70, from the soot, prepared in accordance with the procedure described in Paragraph 12 herein in a helium atmosphere until a thin film was formed on the surface of the quartz substrate. According to the procedure described therein, he removed the film from the quartz substrate and took the UV spectra of the collected material. As outlined in the notebook he continued subliming the material in the soot until another film appeared, which, he again isolated and scanned. He repeated this process until no more material was collected on the quartz substrate. It is noted that in the spectrum located on the right side of Page B-3, there are blue and red lines which show absorption at about 230, 270 and 340 nm. These absorptions turned out to be associated with and reflective of the presence of fullerene-60 and fullerene-70 in the sample. This again is illustrated by the blue and the red lines in the spectra located on the left side on page B-4.

17. Exhibit C is a photocopy of 9 pages of my notebook, identified as C-1 to C-9. These pages describe the vaporization of carbon in an inert atmosphere to form the carbon sooty product, as described herein, the isolation of the carbon soot and separation by sublimation of the fullerenes, e.g., fullerene-60.

18. Prior to any sublimation, I took the UV of the sample of carbon soot produced and isolated from the sides of the chamber in accordance with the procedure described herein. The UV confirmed the presence of fullerene species, e.g., fullerene-60, <sup>in</sup> the soot.

19. Pages C-1 to C-5 describe various separations of fullerene-60 from the collected soot by sublimation. Attention is directed to Pages C-4 and C-5, which not only describes a sublimation of the fullerene-60 from the soot, but also provides the spectra showing the camel humps referred to hereinabove, respectively. This spectra clearly evidence that the product contained fullerene species, e.g., fullerene-60.

20. Pages C6 and C7 describe additional sublimation experiments that were used to separate the fullerene-60 produced in macroscopic amounts from the soot. In the experiments described therein, a 1cm x 2cm microscope slide which had been heavily coated with carbon soot in accordance with the procedure described in paragraph 12 hereinabove, was heated. The heating was effected in a small quartz crucible surrounded by tungsten wire in the bell jar filled with about

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one atmosphere of helium. The quartz substrate was placed just above the crucible for collecting the sublimed material. To prove that I had prepared the fullerene-60 in macroscopic amounts, I performed several sublimations and scanned the sublimed product each time. A typical UV is provided on Page C-9.

21. The UV spectra on page C-9 clearly shows the presence of the camel humps, and this clearly indicates that fullerene-60 was produced by the process described hereinabove.

22. Exhibit D is a photocopy of two pages of a laboratory notebook of Lowell Lamb. The sooty carbon product comprising macroscopic amounts of fullerene-60 was prepared as above. The isolation of a fullerene species, e.g., fullerene-60, from carbon soot and the purification of same, was effected by sublimation. Attached to the bottom of Page D-1 and Page D-2 is the UV and visible spectra, respectively, of the fullerene-60 product so obtained.

23. On the graph on the bottom of Page D-1, attention is drawn to the UV absorptions at 240, 270 and 340nm again indicating the presence of fullerene-60 in the sample.

24. Exhibit E is a photocopy of three pages of Lowell Lamb's laboratory notebook. Page E-1 is a visible spectra of fullerene-60, prepared in accordance with the procedure described hereinabove and shows absorption at about 415, 500, and 670nm, which is indicative of fullerene-60.

Page E-2 describes modifications of the procedure described on Page 92 and 93 of the notebook (Pages B-1 and B-2). Moreover, it refers to an IR spectrum of fullerene-60 on NaCl produced in accordance with the procedure outlined on Pages B-1 and B-2. It refers to the absorption of the fullerene-60 at 1410 and 1180 cm., which turns out to be associated and reflective of the presence of fullerene-60. Page E-3 is a copy of IR spectra of fullerene-60 on NaCl referred to on Page E-2.

25. Exhibit F is a photocopy of relevant portions of a progress report which was written in Lowell Lamb's laboratory notebook. Page F-3 comments on the IR and UV spectra of the fullerene-60 sample obtained and reports that the procedure described in Exhibit B produces a fullerene-60 product in approximately 0.1 gram batches.

26. The fullerene products, produced in accordance with the procedure described hereinabove, were soluble in non-polar solvents and insoluble in polar solvents. This is indicated in Exhibit G, which is a photocopy of two pages of my notebook.

27. Exhibit G consists of two pages, Page G-1 and G-2. Page G-1 describes the tests which I conducted regarding determining the solubility of the fullerene product. I found that it is soluble in benzene, CS<sub>2</sub>, and CCl<sub>4</sub>, but insoluble in water, acetone, methanol and propanol.

28. The fact that the fullerene product is found to be soluble in non-polar solvents, while the soot was insoluble in the non-polar solvent was evidence that non-polar solvents could be used to extract the fullerene product from the soot. Thus, this represented an alternate means for separation of the fullerene product from the soot.

29. Page G-2 is the UV/VIS spectrum of the fullerene product dissolved in benzene.

30. The spectra referred to in paragraphs 21 and 29 are of exceptional quality and clearly show the presence of fullerene-60.

31. Exhibit H consists of one page and is an X-ray diffraction of the fullerene powder produced in accordance with the procedure described hereinabove. The spectrum is identical to the ones we and others published with respect to fullerene-60.

32. Exhibit I, consisting of one page, is a mass spectrum of the fullerene material produced in accordance with the procedure described hereinabove. It clearly shows the presence of two species of fullerenes, e.g., fullerene-60 (mass 720) and fullerene-70 (mass 840) in a single ionization, along with some breakup products of fullerene-60 such as doubly ionized fullerene-60.

33. These exhibits demonstrate that a process for the preparation and isolation of various fullerene species, e.g., fullerene-60 and fullerene-70 as species of fullerenes,

in macroscopic amounts has been performed by myself or under my direct supervision and control in the United States prior to the publication date of Kratschmer et al.

34. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated:

May 10, 2000

Donald R. Huffman  
DONALD R. HUFFMAN

MJC:ahs/bb

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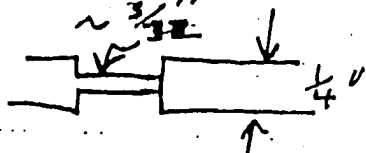
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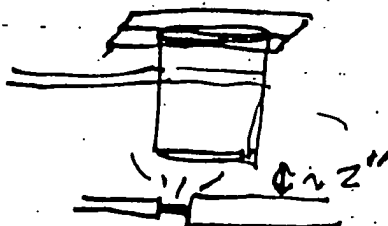
# Journal Entry

In the last three days, I've made some progress in the production of  $C_{60}$ . Below is the process.

- ① Evaporate Carbon in  $\sim 100$  Torr of He\*. The tip dimensions are



Above the rods I have a "chimney" made out of a  $\sim 2$ " diameter quartz tube topped with two microscope slides to collect the smoke



\* Flush 3 times with  $\sim 100$  Torr of He,  
First

Set the variac to  $\sim 75$ ; if the tip breaks at ~~two~~ thin sections connect the  $1/4$ " rods, turn the voltage to 85.

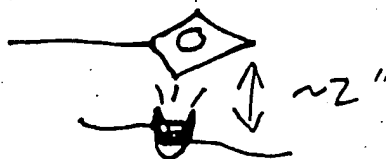
- ② Repeat  $\sim 5$  times.
- ③ Scrape smoke off chimney + sides of chamber.
- ④ Combine smoke + benzene in a test tube. Stir thoroughly.
- ⑤ Ultrasonic for  $\sim 2$  min.
- ⑥ Centrifuge on 4 for  $\sim 10$  min.
- ⑦ Pour Dark red liquid into quartz crucible - place crucible on warm hot plate (cool enough to be touched for a few seconds) and heat until all benzene has evaporated. A brownish golden residue should remain.

READ BY JAMES J. COMEST

25

EXH. B-1

- (8) Put crucible with residue into wire basket in vacuum chamber.
- (9) Flush 3 times with 100 Torr of He - At 100 Torr of He, sublime  $C_{60}$  onto quartz substrate at  $\sim 30$  V on Variac until film appears on substrate.



- (10) Remove substrate + scan from 400-200 nm.
- (11) <sup>clean substrate and</sup> Repeat (9) & (10) until all of the other volatiles have been driven off. This will have happened when the spectrum resembles the brown spectrum taped in on page 94. The blue and purple spectra are of samples which still contain this unknown volatile. What remains in the crucible is  $C_{60}$ .

### Temperature Dependence

Four  
Taped in on page 95 are ~~three~~ scans of a  $C_{60}$  sample

- (1) Blue - Room Temperature
- (2) Green - Immediately after immersion & equilibration in liquid  $N_2$ .
- (3) Purple - 2nd  $N_2$  Temp scan
- (4) Red - Final Room Temp scan.

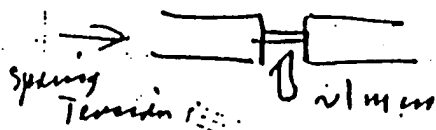
Broad feature (features?) in visible range  
425-525 nm appear real.

READ BY JOHN T. FRANKS  
for J.E.D.

## Co making

REDACTED

10:40 AM - Temp  $\approx 100^\circ\text{C}$   $\approx 380^\circ\text{F}$  as gauge  
according to calibration in Lowell's notebook



#1 UV spectrum on Cary 118 shows  
a good Co spectrum just as in and before.

Peak OD  $\approx 1.4$

Scraped off with sand blaster glassine paper.

#2 UV spectrum shows similar results

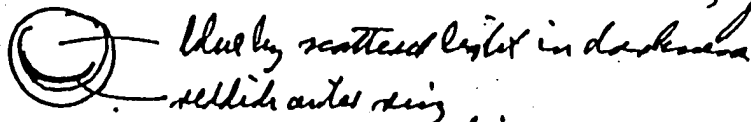
Peak OD  $\approx 2.25$ . In this procedure I prohibited the  
robots allow the usual smell of lead temperature  
stuff to come off & disappear

Used samples #1 & #2 scraped off to try to sublimate Co.



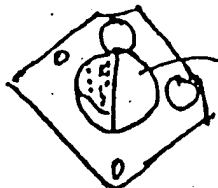
Multistandard tungsten wire coil solvent carefully into a shape  
that would hold a clear quartz crucible.

Notes to about Co in vacuum & then something, just



blue by scattered light in darkness  
reddish outer ring

UV spectrum is excellent until better background is seen



wipe off right side of sample  
take to do spectra of clean vs dirty

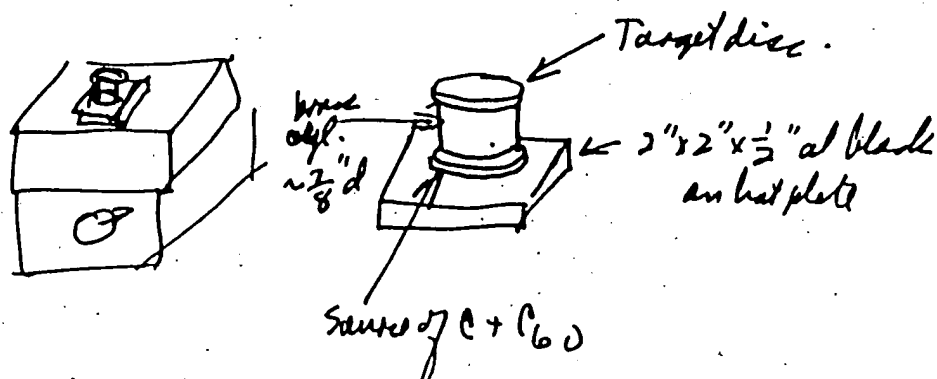
(cont.)

74

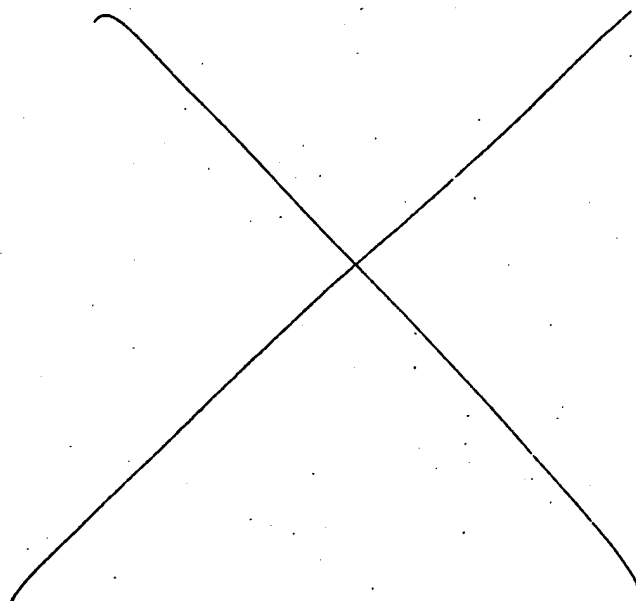
REDACTED

(cont.)

Attempt at Sublimation of  $C_{60}$  in Air  
on Hot Plate.



Heated for 10 min in the above arrangement. No indication of anything on target disc. Re-analysis of UV spectrum of source disc shows change away from  $\pi$  bump structure.



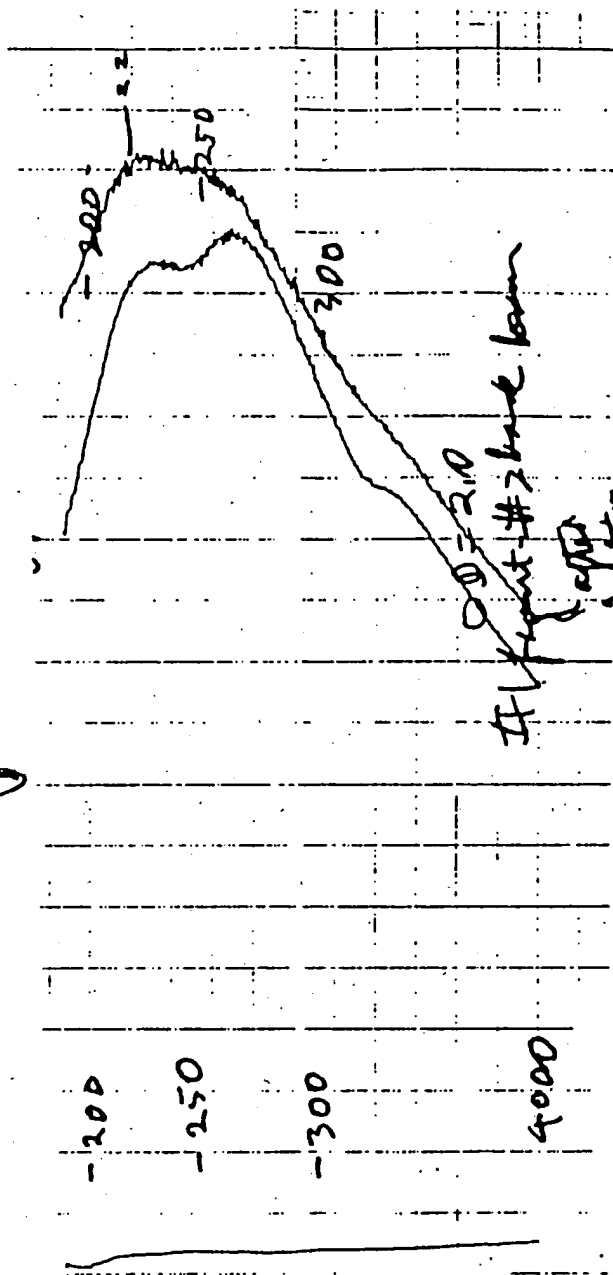
EXH. C-2

See next page

REDACTED

75

(cont.)

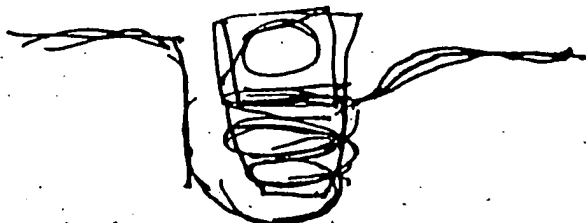




76

(cont.)

For next try at annealing  $\text{C}_{60}$  I wound a new coil around the dense quartz crucible out of 3-stranded tungsten.



Placed ab. holder with silica disc just above the crucible.

Note: perspective of drawing above is not good.

Scraped carbon off the sample holder from a previous run -- also collected same by scraping from posts and other hardware in the chamber.

Flushed chamber w/  $\text{He}$  & filled to  $\sim \frac{3}{4}$  atm. Heated filament  $\sim 15$  amp until I observed something on disc.

Spectrometer opposite page  
shows that I indeed succeeded in concentrating  $\text{C}_{60}$ .

The sample again appeared bluish by scattered light in the forward direction and perhaps reddish by transmission. There were some flashes of the fluffy carbon that seems to have marked the surface.

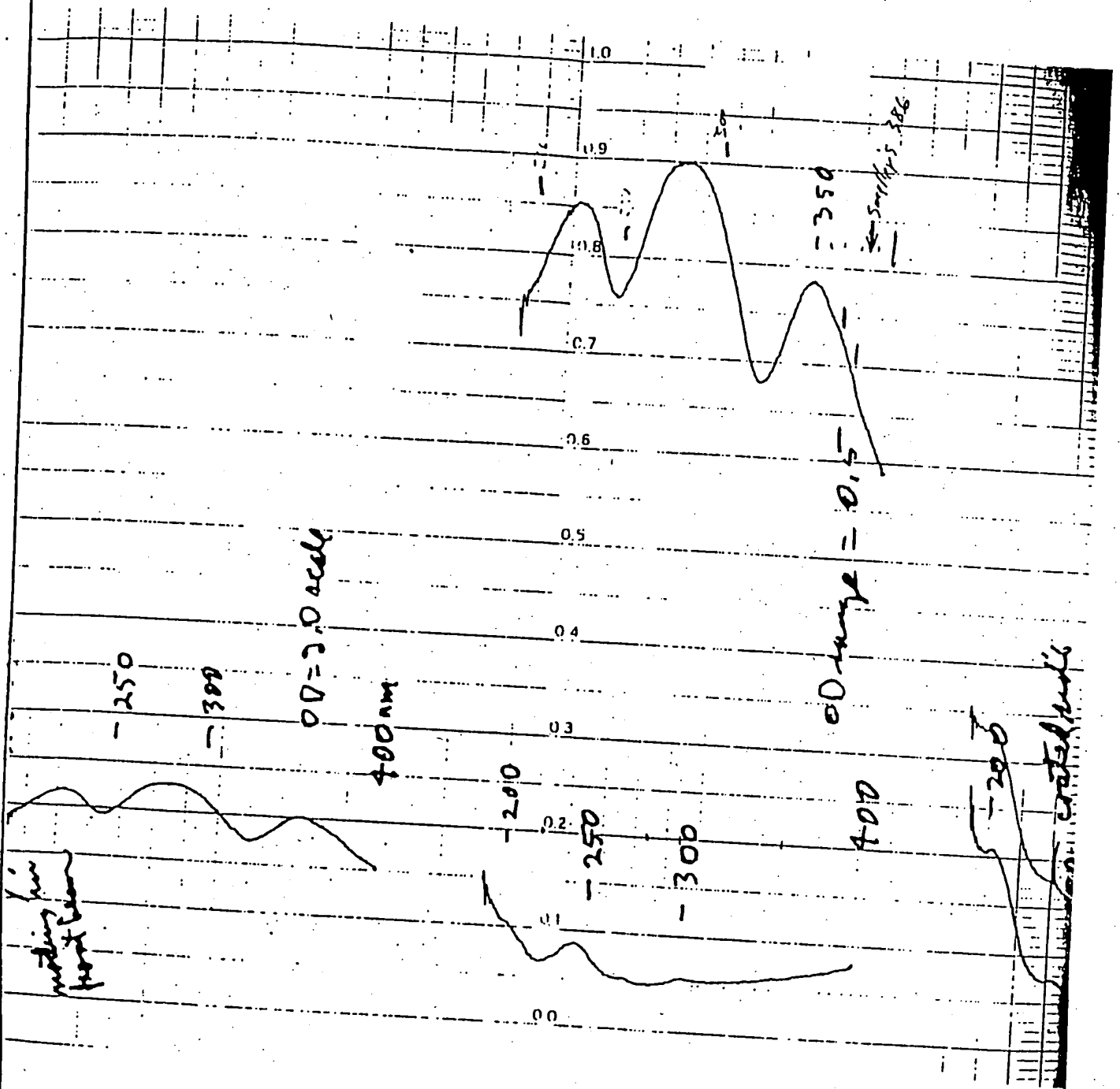
I will try to get around this by not scraping off the carbon into fluffy aggregates.



Fluffy carbon

REDACTED

77

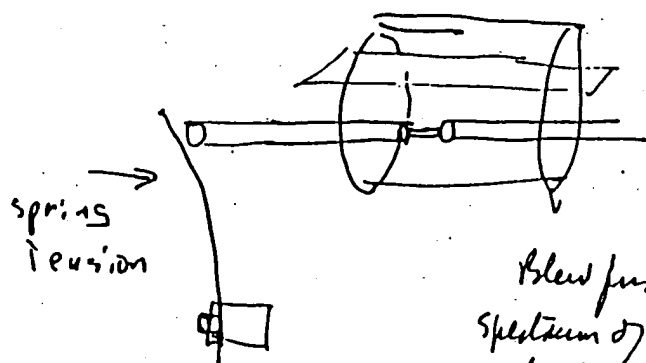


EXH. C-5

78

# More C<sub>60</sub> making

#1 Trial 3mm diameter rod in qtz. tube w/ microscope glass as shown below:



3mm is  
Blow from the large.  
Spectrum of stuff inside shows  
material C<sub>60</sub> signature.

## #2 Trial

Same ring as above but 1 1/2 in diam. rod, a little longer than usual (~1cm). Rod snapped when heating started but sample continues as shrapnel part was pushed by spring against stuff.

Heavy coating on inside of ring & on slide. Will log again with a 1/2 mm x ~8 mm tip to get more C<sub>60</sub>. Then log to concentrate it.

## #3 Trial

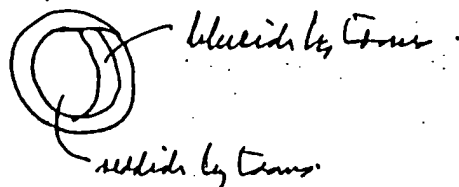
Heated rather quickly. Tip collapsed. ~5 sec in all to try to prevent draining off the C<sub>60</sub>.

#4 Microscope slide from #2-3 with heavy coating is broken into a few pieces to fit into crucible. Idea is to try to prevent the fluffy contaminant from yesterday by subliming directly from coated slide.



cont.

Heated filament to ~ 10 amp on meter. Filament misbehavior. Heating most toward substrate. later settled down as that emission all heating occurred. 40 amperes - 20 on current meter. Left it for ~ 3 min while I observed deposition using microscope light from above.



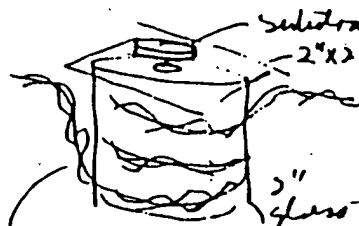
Two spots resulted. No spectrum yet. Totally different. Don't understand the bluish by trans. part.

Cleaned substrate - will now try same charge as done on (chamber) to see if any  $C_{60}$  is left.

Card. 3 min - 30 v - 12.5 amp on primary. Apparently no more red or small dark patches & holes in chamber as viewed by microscope. Charge into chamber in darkness now. No evidence of any more  $C_{60}$  or anything else deposition on substrate.

Now try an unheated portion (4 cm x 1 cm) of heavily coated microscope slide (#1 & #2). Initial power more gradually. at 26.5 v & 11 amp primary current I see spots of coating develop on substrate. Also observe smoke in the chamber.

Now try the large (2") cylinder with heavy coat wire

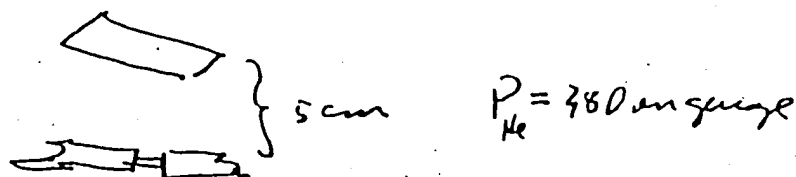


Results - Nothing got there the 1/4" hole in 2x2 glass to substrate.

3 rounded targets heated. Various spectra on charts. 2" x 2" have some coating of blue & red.

80

Try standard condition to make being 60 amole.

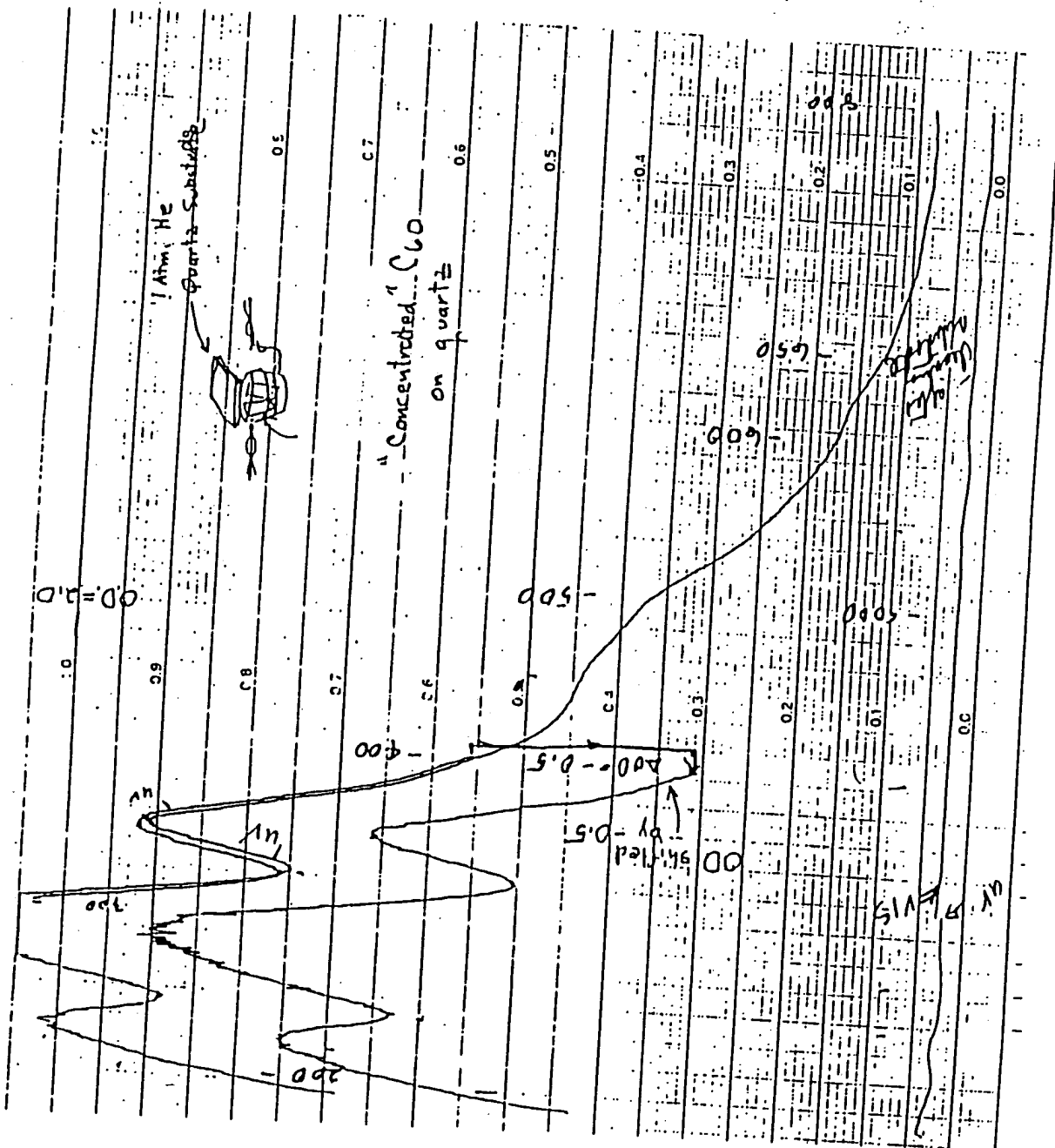


Today I faxed to Wolfgang a copy of the spectrum of  
 Pt which ~~is~~ a copy is shown on the attached page.

There appears to be structure in the region between about  
 4500 Å and 7000 Å which is real. The curve of  
 course shows why the material is reddish brown.

To W. Krätschmer

Spectrum of  
"concentrated" smoke

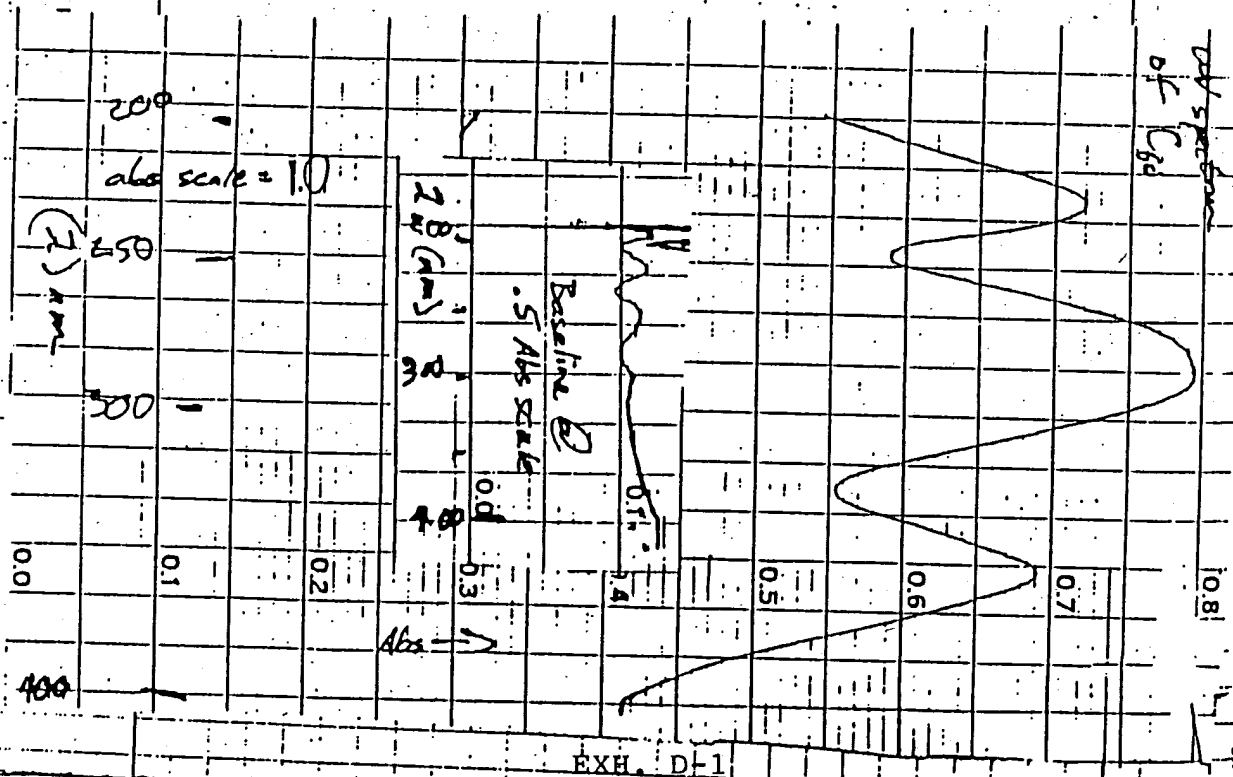


C<sub>60</sub>

Today I made smoke + concentrated C<sub>60</sub> using sublimation.  
 Taped in below is the UV scan of the sample,  
 and taped in on page 91 is the Visible scan.

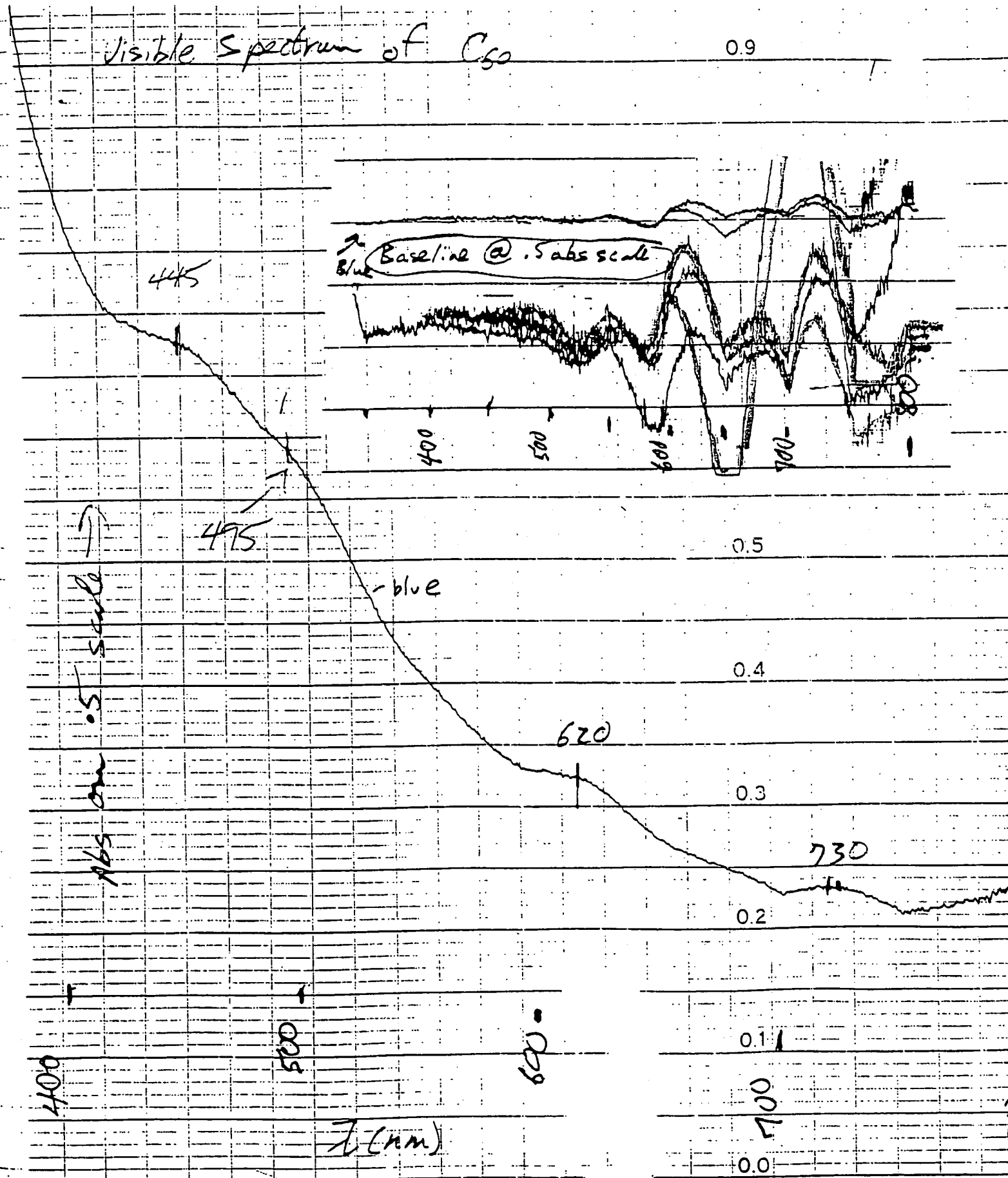
There appear to be 4 absorption features superimposed  
 on the broad carbon feature in the visible. The 620 nm  
 and 730 nm may be instrumental error (see baseline).  
 The 445 and 495 are close to the 4428 Å and  
 4882 nm DIB.

The Electron



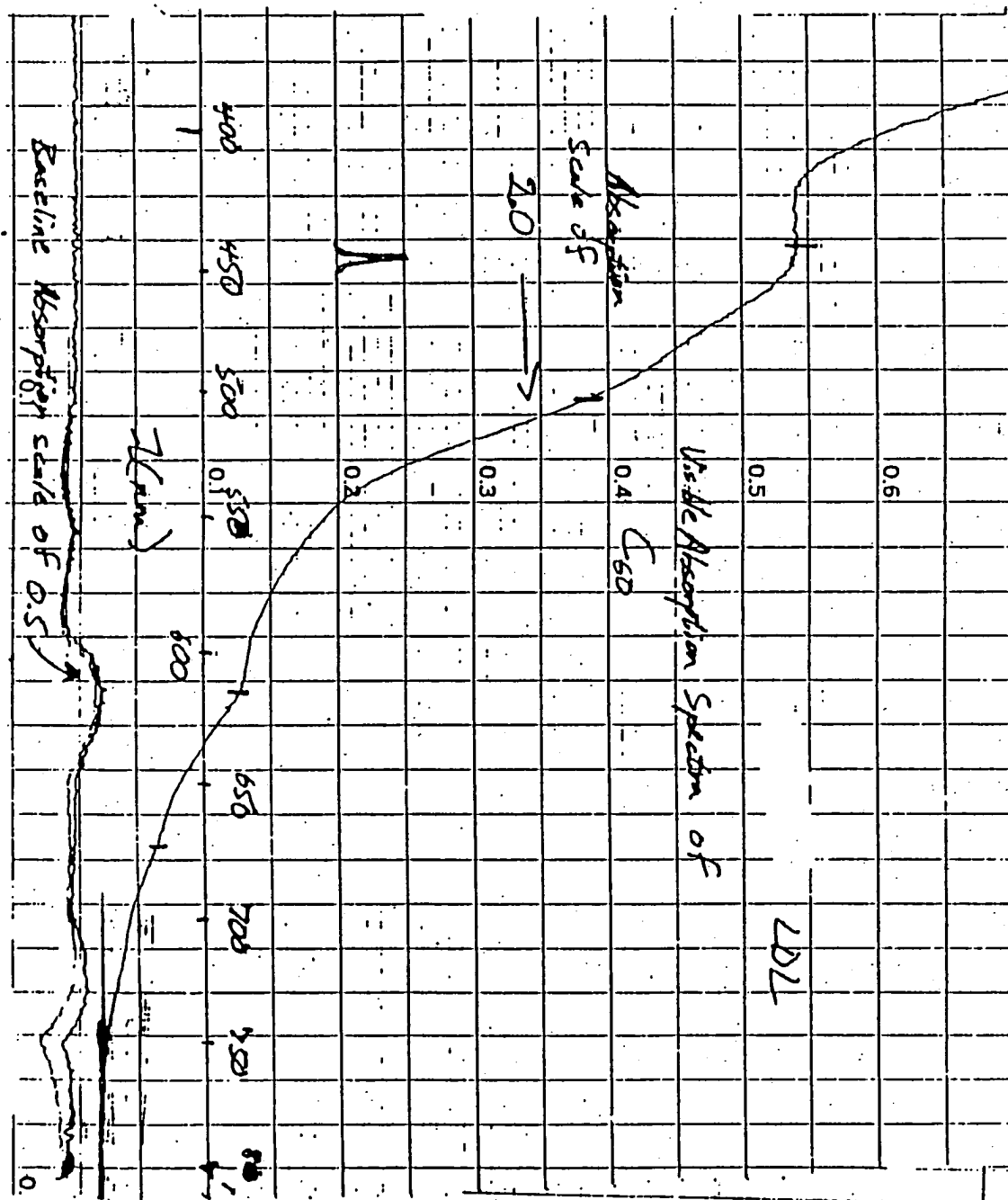
Visible Spectrum of C<sub>60</sub>

0.9





Taped in below is a visible spectrum of  $C_{60}$ .  
 I see features at 445, 500, 670, and possibly 620 nm.  
 These may correspond to the 4428, 4882, 6660, and 6200 Å  
 DIB.



~~Modifications~~ Modifications to Shroff's Production Method on pages 92 & 93.

Step ① - Tip diameter  $\sim \frac{1}{8}"$

Step ② - Substrate - Crucible separation  $\sim 2 \text{ mm}$

### Questions

① Why am I only seeing some of the DIB's? Specifically, why am I not seeing the 5800 Å feature?

#### Answer A

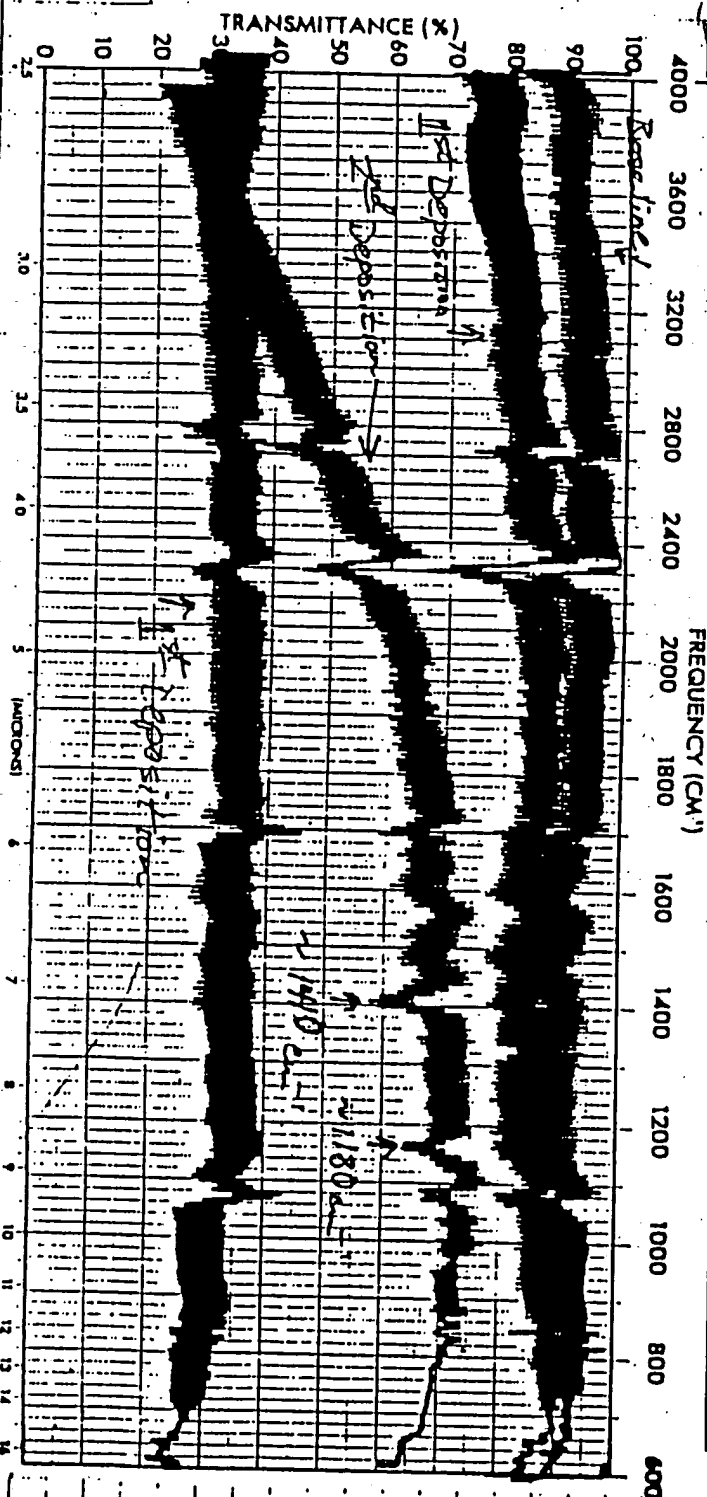
I am only seeing pure carbon and/or carbon 60 with a trapped He feature. The other DIB's are due to  $C_{60}$  with various ions trapped inside.

#### Answer B

The other DIB's are due to  $C_{70}$ ,  $C_{90}$ , ...

Taped in on page 98 is an IR scan of  $C_{60}$  on NaCl. Careful comparison of the baseline to the absorption spectrum shows only two features - at  $\sim 1410$  &  $1180 \text{ cm}^{-1}$ . These match up well to the Kratichner et al features at ~~1429~~  $1429$  and  $1183 \text{ cm}^{-1}$ . In his paper this morning, he states that they are still seeing contamination due to C-H at  $2900 \text{ cm}^{-1}$ . I don't see that in my spectrum, so either it is not present or the instrument is not sensitive enough.

REDACTED

IR spectra of  $C_{60}$  on NaCl

EXH E-3

REDACTED

Progress Report

REDACTED

#### IV UV-Visible

I have obtained good spectra of  $C_{60}$  from about 200-700 nm using the CARY 118. Scans are taped in on pages 90, 91, 96. I see visible features at 445, 500, 670, and possibly 620 nm.

#### V IR Spectra

An IR scan from 4000-800  $\text{cm}^{-1}$  is taped in on page 98. I see the two features at 1429 and 1183  $\text{cm}^{-1}$  and no other features. There seems to be relatively little contamination.

#### VI Near IR

Using the CARY 14, I've made some preliminary scans from 600-1600 nm. There is really only one candidate feature - at 1280 nm - but I don't have a baseline yet.

#### VIII $C_{60}$ Production

The most important thing I've done is refine our method for  $C_{60}$  production. I would estimate that we are now able to make it in ~0.1 gram batches. The purity appears to be very high.

REDACTED

REDACTED

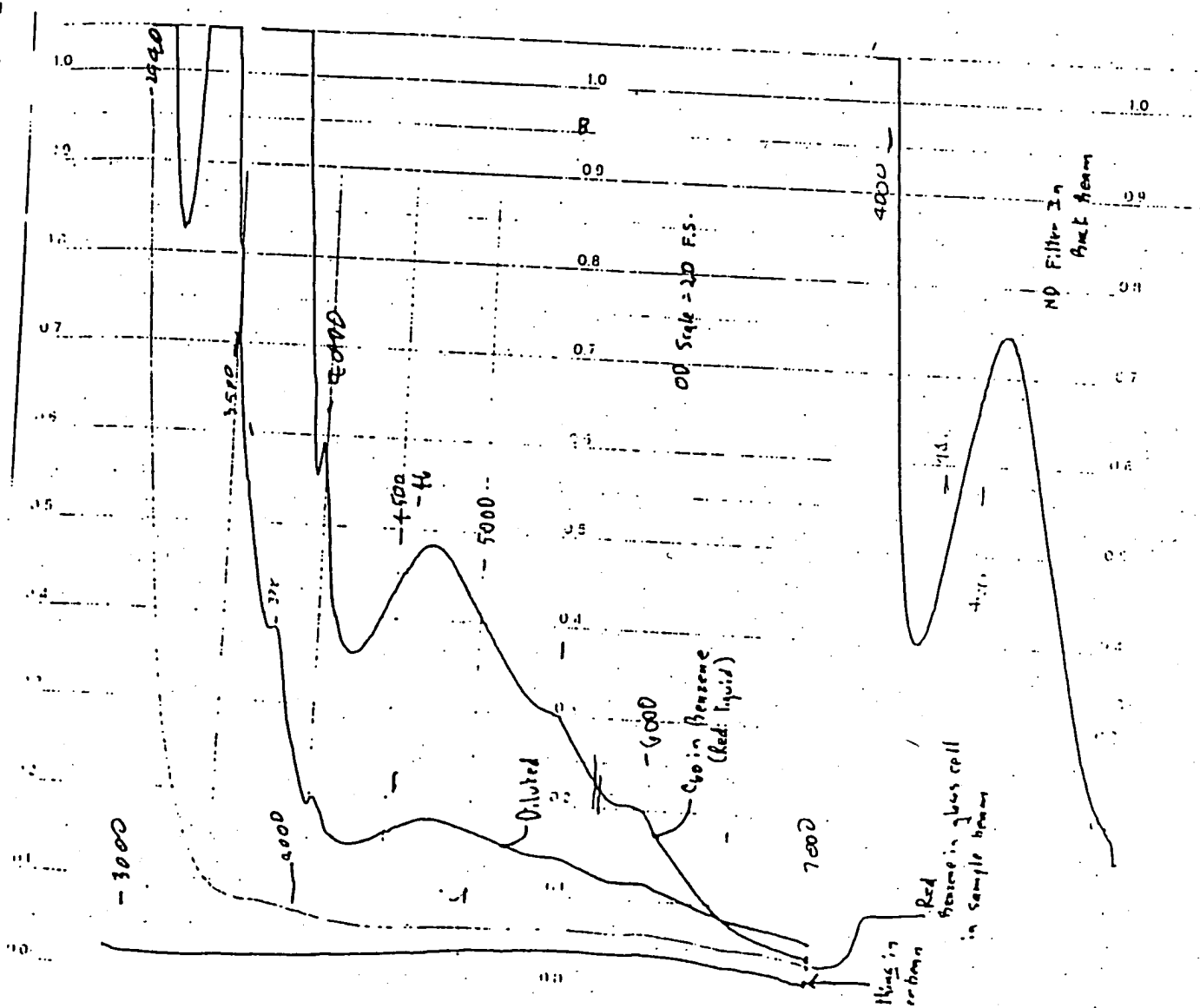


REDACTED

89

Ran a spectrum of  $\text{Co}$  in benzene.  $\rightarrow$  See attached page -  
Saturdays

Came to lab about 3:00 P.M. Tried various  
solvents for  $\text{Co}$ . Successes with  $\text{CS}_2$  and  $\text{CCl}_4$  with a moderate  
apparent success for benzene. Failures included water,  
acetone, ethanol, methanol, propanol.



The above spectrum was measured on